11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO_2-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_2-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see Section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.4 Repeat the procedures outlined in Sections 11.2 and 11.3 for each sample and each blank.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_2^-/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO_2^-concentration using the calibration curve obtained in Section 10.4.

NOTE: Some test tubes give a high blank NO_2^- value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, Section 11.4.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature.

B = Analysis of blank, μg NO_2^-/ml.
C = Concentration of NO_X as NO_2, dry basis, mg/dsm^3.
E = Column efficiency, dimensionless
$K_2 = 10^{-3}$ mg/μg.
m = Mass of NO_X, as NO_2, in sample, μg.
P_{bar} = Barometric pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
s = Concentration of spiking solution, μg NO_3/ml.
S = Analysis of sample, μg NO_2^-/ml.
T_m = Average dry gas meter absolute temperature, °K.
T_{std} = Standard absolute temperature, 293 °K (528 °R).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_m = Dry gas volume as measured by the dry gas meter, scm (scf).
x = Analysis of spiked sample, μg NO_2^-/ml.
X = Correction factor for CO_2 collection = $100/(100 - \%CO_2(V/V))$.
y = Analysis of unspiked sample, μg NO_2^-/ml.
Y = Dry gas meter calibration factor.
1.0 ppm NO = 1.247 mg NO/m^3 at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m^3 at STP.

1 $ft^3 = 2.832 \times 10^{-2}$ m^3.

12.2 NO_2 Concentration. Calculate the NO_2 concentration of the solution (see Section 7.2.11) using the following equation:

$$\frac{\mu g\ NO_2^-}{ml} = g\ NaNO_2 \times \frac{\text{purity, \%}}{100} \times 10^3 \times \frac{46.01}{69.01} \qquad \text{Eq. 7C-1}$$

12.3 NO_3 Concentration. Calculate the NO_3 concentration of the KNO_3 solution (see Section 7.2.12) using the following equation:

$$\frac{\mu g\ NO_3^-}{ml} = g\ KNO_3 \times \left(10^3\right) \times \frac{62.01}{101.10} \qquad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(std)} = V_m\ X\ Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \qquad \text{Eq. 7C-3}$$

$$= K_1\ X\ Y\ V_m \frac{P_{bar}}{T_m}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units.
K_1 = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200\ (x-y)}{1.0\ s\ \frac{46.01}{62.01}} = \frac{269.6\ (x-y)}{s} \qquad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.
1.0 = Volume of spiking solution added, ml.
46.01 = µg NO_2^-/µmole.
62.01 = µg NO_3^-/µmole.

12.6 Total µg NO_2.

$$m = 200\left(\frac{500}{50}\right)\left(\frac{1000}{100}\right)\left(\frac{(S-B)}{E}\right) = \frac{(2\times10^4)(S-B)}{E} \qquad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.
50 = Aliquot of prepared sample processed through cadmium column, ml.
100 = Aliquot of $KMnO_4$/NaOH solution, ml.
1000 = Total volume of $KMnO_4$/NaOH solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Eq. 7C-6}$$

13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_X, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.